

In Situ Uranium Bioimmobilization: Reduction vs. Reoxidation

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Push-pull test publications available at:

www.ccee.oregonstate.edu/~istokj/grl-main.htm

S-3 Ponds – ORNL



Site Groundwater

	GW835 (μM)	FW021 (μM)
pH	6.4	3.3
Tc (pM)	410	18000
U	5	6
Ag	1	0
Al	0	12000
As	1	0
Ba	0	10
Be	20	0
Bi	0	0
Br ⁻	150	0
Ca	3500	19000
Cd	0	4
Cl ⁻	650	7900
Co	1	46
Cr	1	0

	GW835 (μM)	FW021 (μM)
Cs	0	0
Cu	1	9
Fe	4	4
Ga	1	0
K	120	980
Mg	1100	8300
Mn	50	2500
Na	1100	23000
Ni	1	220
NO ₃ ⁻	1200	140000
Pb	0	0
Se	1	1
Sr	4	22
SO ₄ ²⁻	830	430
Zn	1	48

Bioimmobilization

Trace U(VI), Tc(VII)
Low pH
High Ca, Al, Mg, etc.
Very high NO_3^-
Moderate SO_4^{2-}

Heterogeneous
High sorbed U(VI)
Aerobic/oxidizing
Microbial activity electron donor limited

Donor Addition →

Denitrification
Iron reduction
Sulfate reduction
 $\text{U(VI)} > \text{U(IV)} \downarrow$
 $\text{Tc(VII)} > \text{Tc(IV\&V)} \downarrow$

Processes Studied In Situ Using Push-Pull Tests

**Site groundwater
amended with
tracer and electron
donor and injected
into existing
monitoring wells**

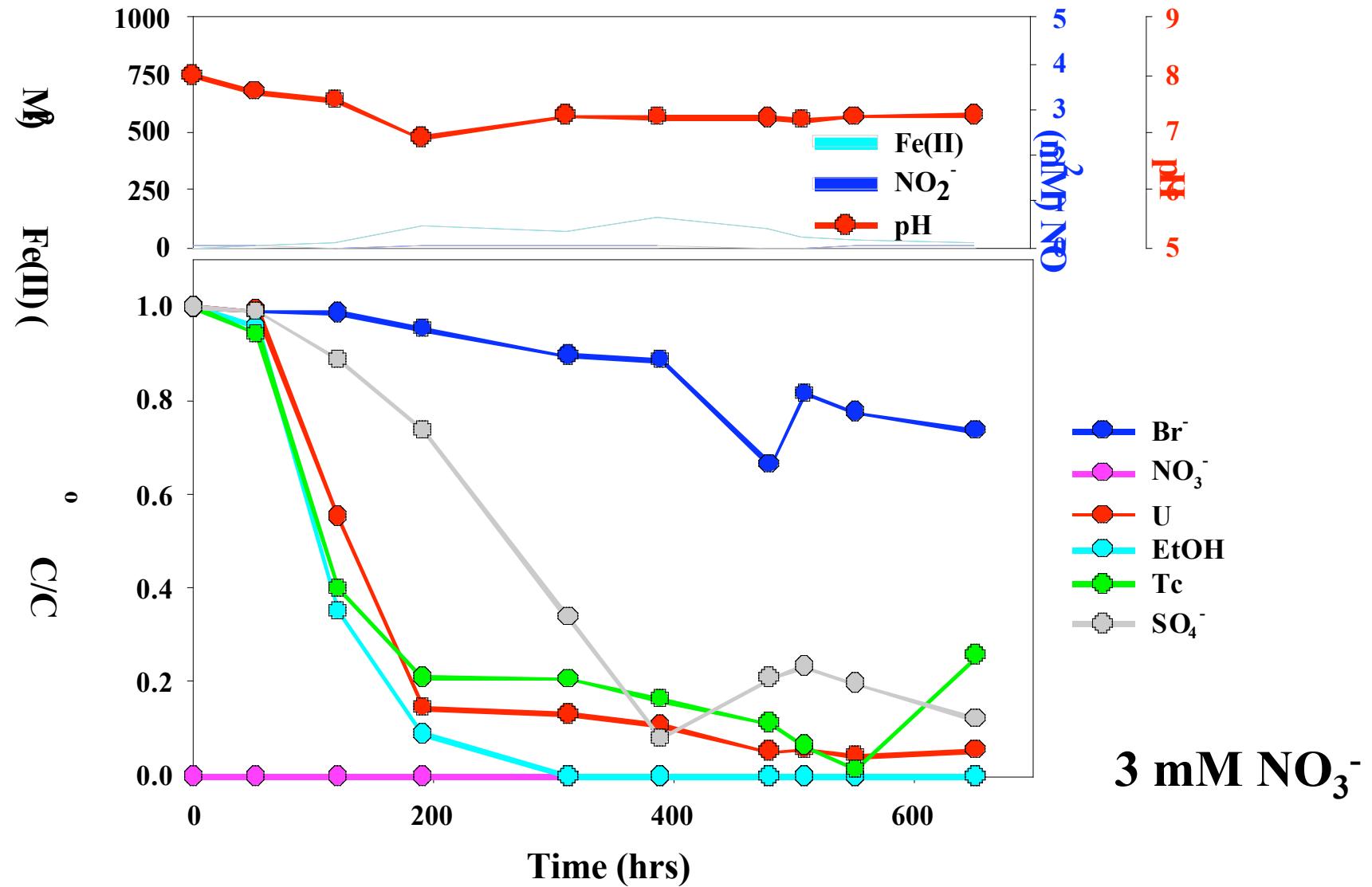


**Composition of
injected test
solution monitored
over time**

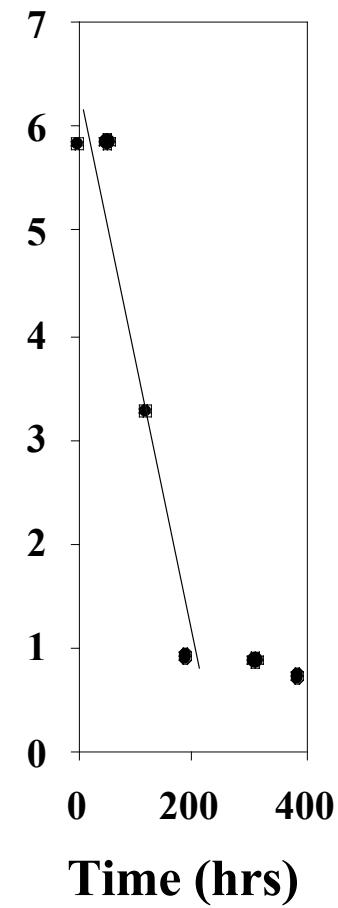
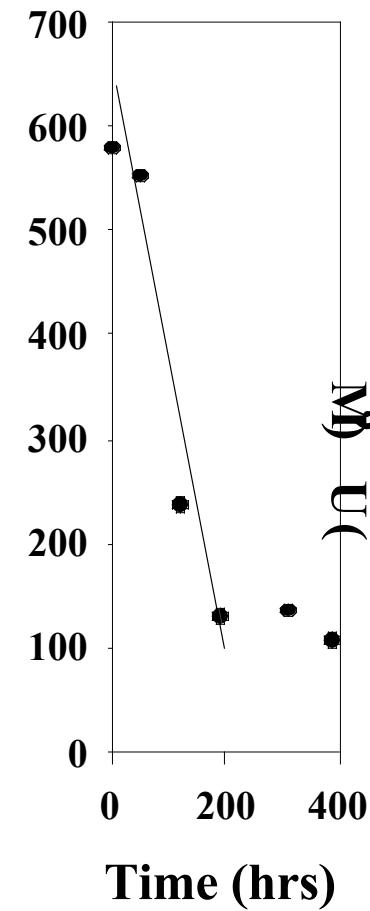
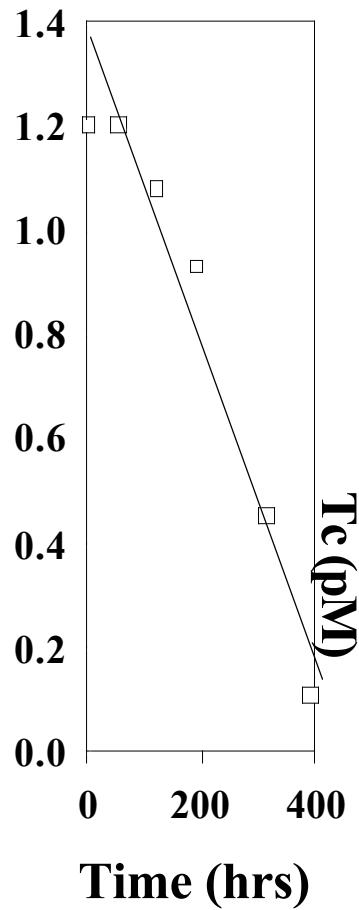
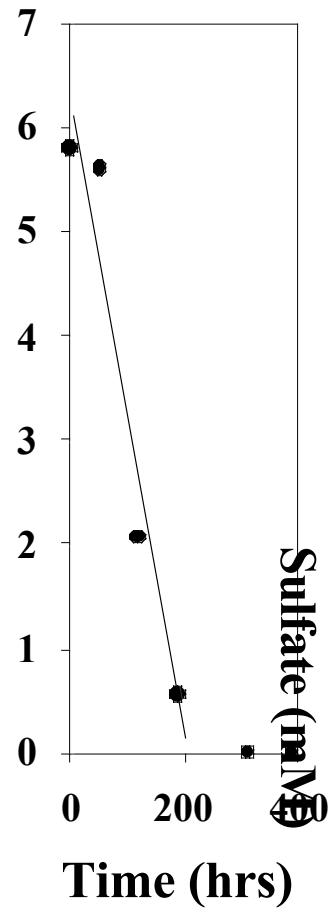


**The
“Dosatron”**

Point 1: It Works ! (at least in short-term)



Point 2: In Situ Rates Can be Quantified



Point 3: Process Effective in Many Sub-environments

Initial Conditions

pH	NO_3^- (mM)	SO_4^{2-} (mM)	U(VI) (μM)	Tc(VII) (pM)
3.3-3.9	100-140	0-1	5-12	10000-15000
5.2-5.6	90-100	0-1	5-12	10000-15000
5.6-7.2	0-6	1-2	1-7	200-1000

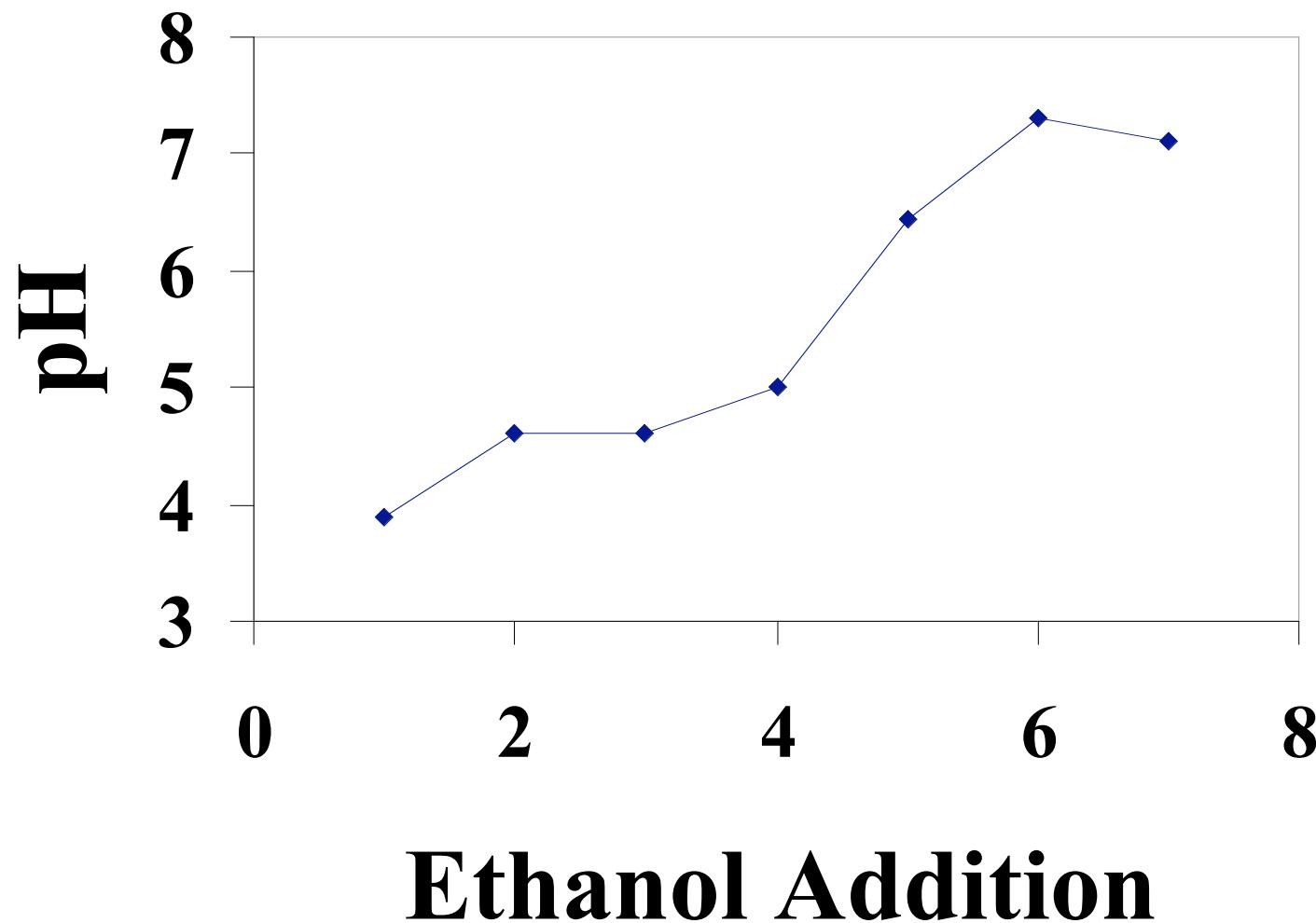
Maximum Rates After Biostimulation

EtOH (mM/hr)	NO_3^- (mM/hr)	SO_4^{2-} (mM/hr)	U(VI) ($\mu\text{M}/\text{hr}$)	Tc(VII) (pM/hr)
0.3-1.0	0.1-0.4	0-0.01	10^{-4} - 10^{-3}	4-30
0.4-8.0	0.3-4.0	0-0.01	10^{-4} - 10^{-3}	10-200
0.1-0.5	0.1-2.0	0-0.03	10^{-4} - 10^{-3}	4-10

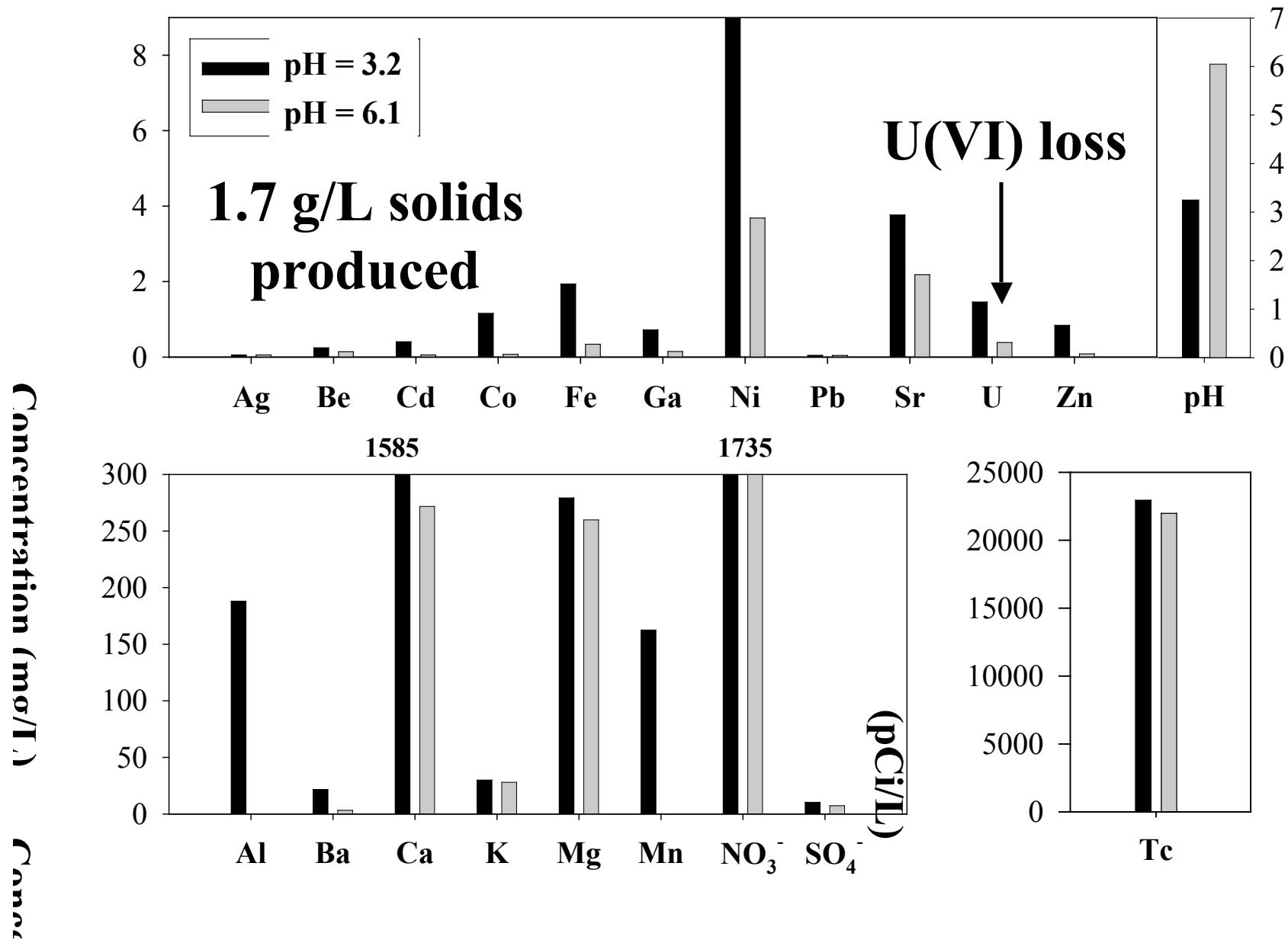
What About the Long-Term ?

- **Biostimulation results in pH increase**
 - Large quantities of precipitates produced
 - Formation of U(VI)-containing solids
- **Most injected electron donor consumed via denitrification**
 - Biomass production
 - N₂ gas production
- **Presence of nitrate and denitrification intermediates can rapidly reoxidize U(IV)**

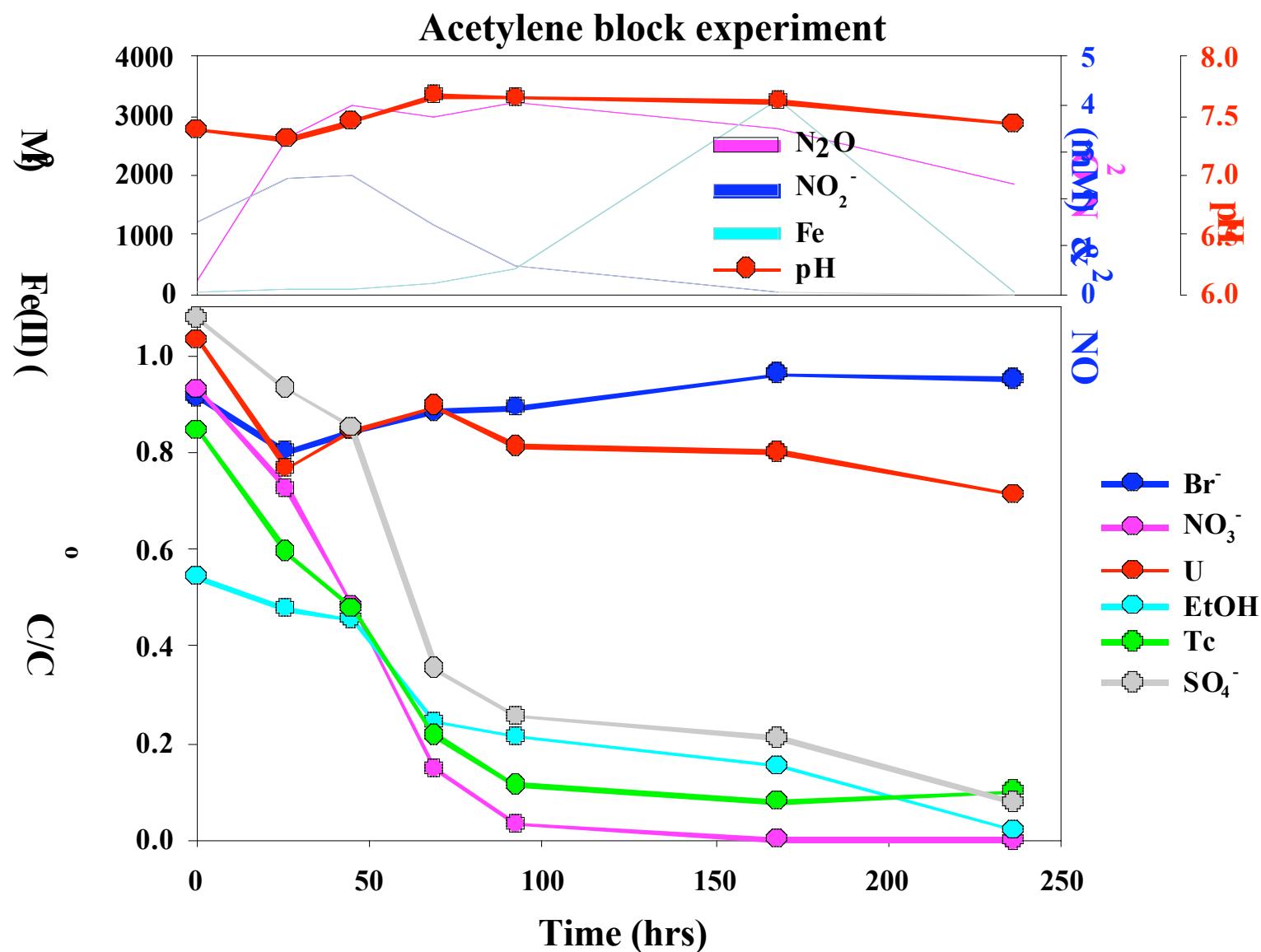
Point 4: Donor Addition Raises pH

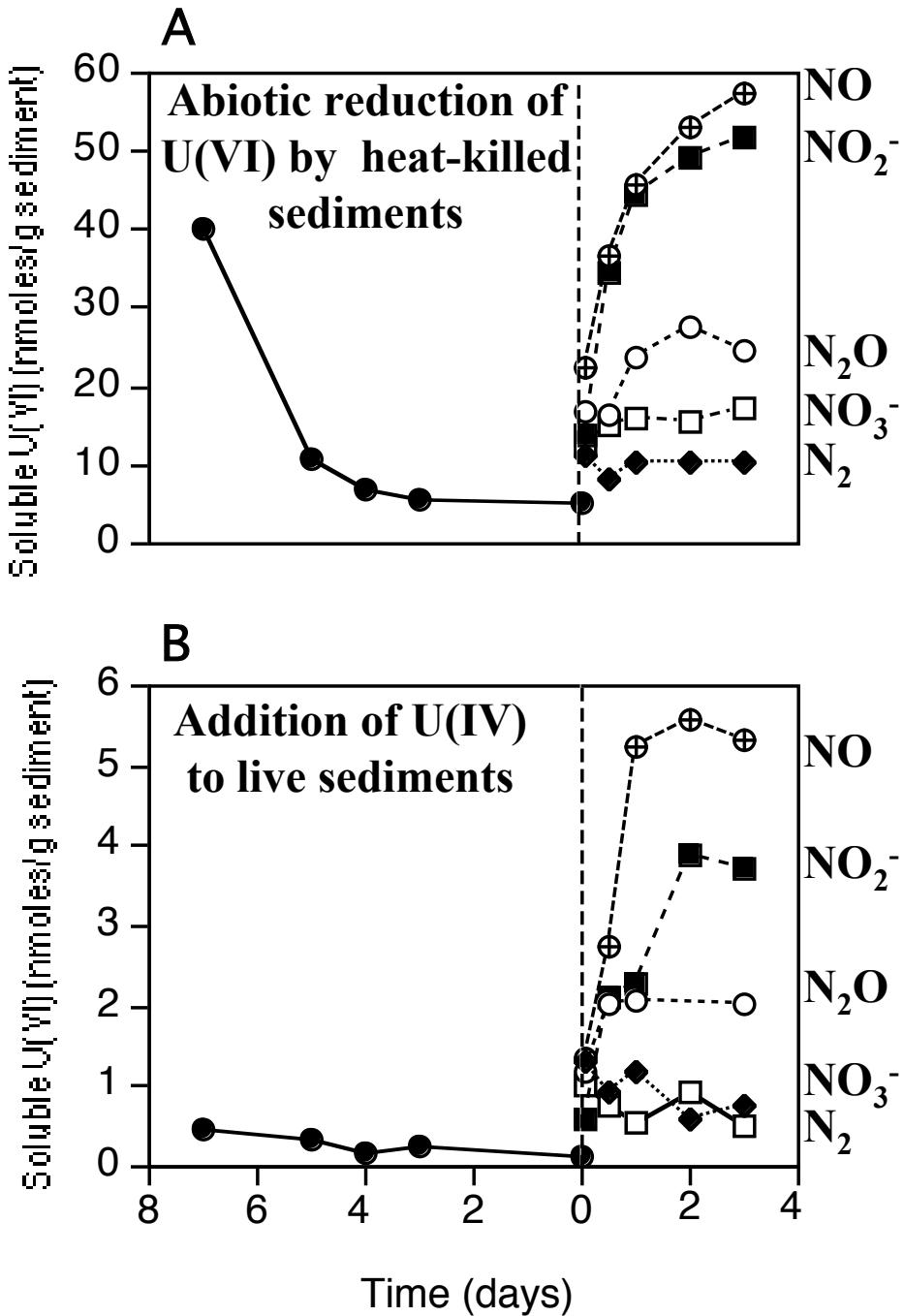


Point 5: Raising pH Changes Composition



Point 6: Denitrification Generates N₂ Gas

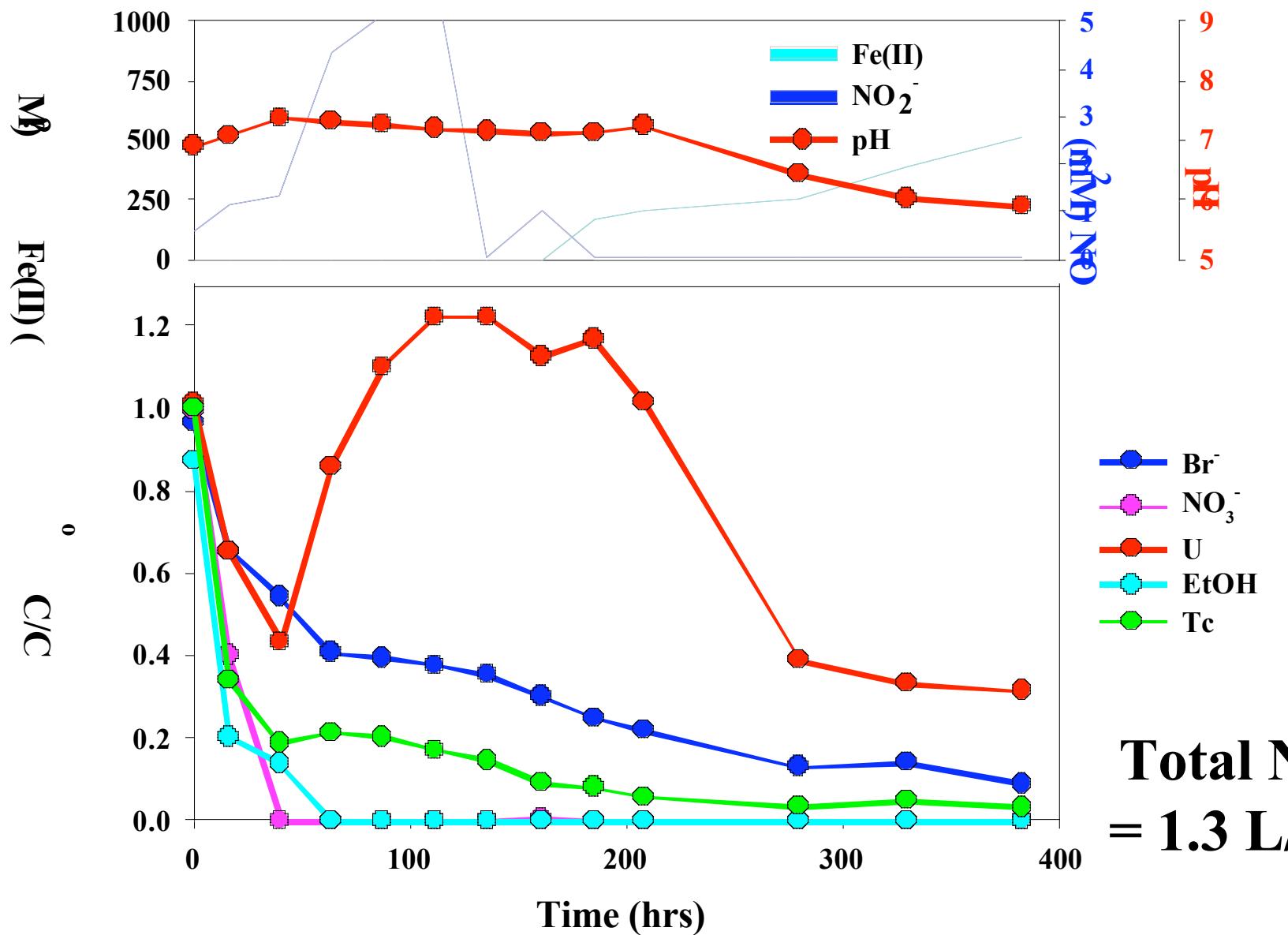




**Point 7: Nitrate and Denitrification
Intermediates Can Rapidly Oxidize U(IV)**

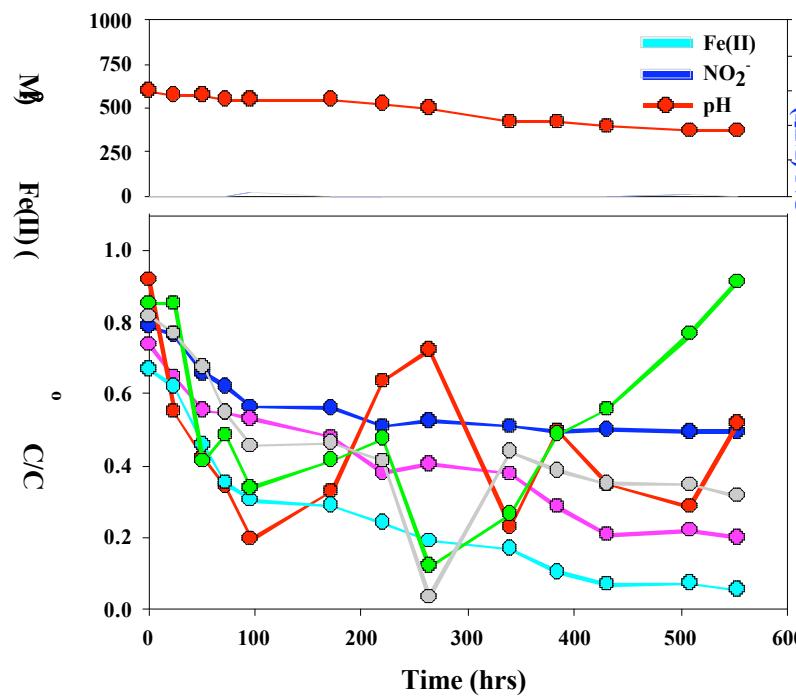
← **Laboratory
incubations**

In Situ Reoxidation of U(IV) During Denitrification ($120 \text{ mM } \text{NO}_3^-$)

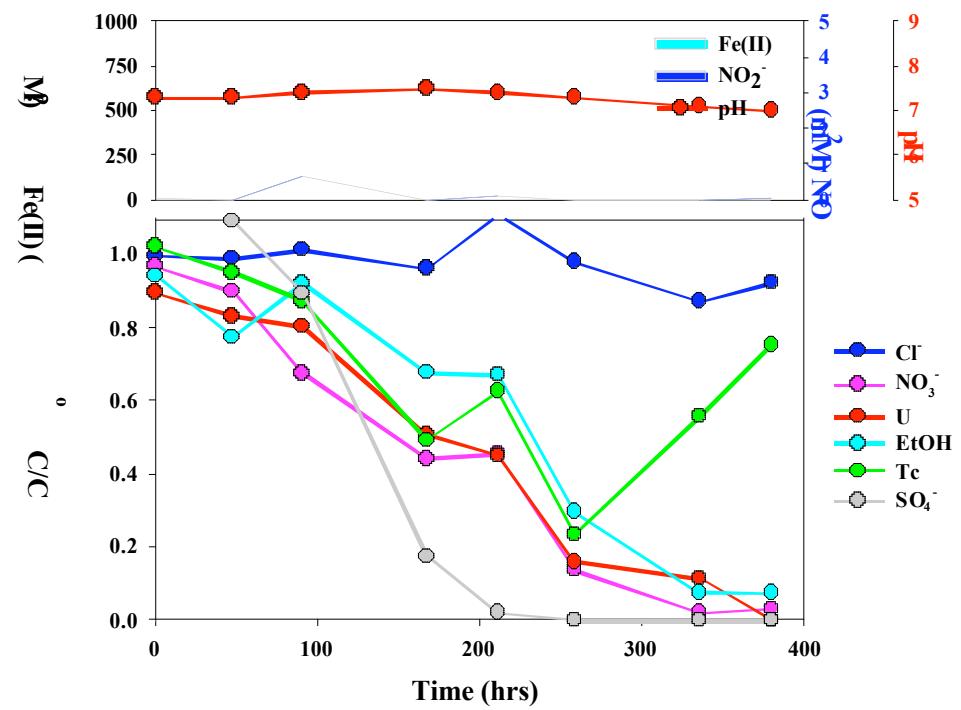


Can Sulfide Mitigate U(IV) Oxidation by Denitrification Intermediates ?

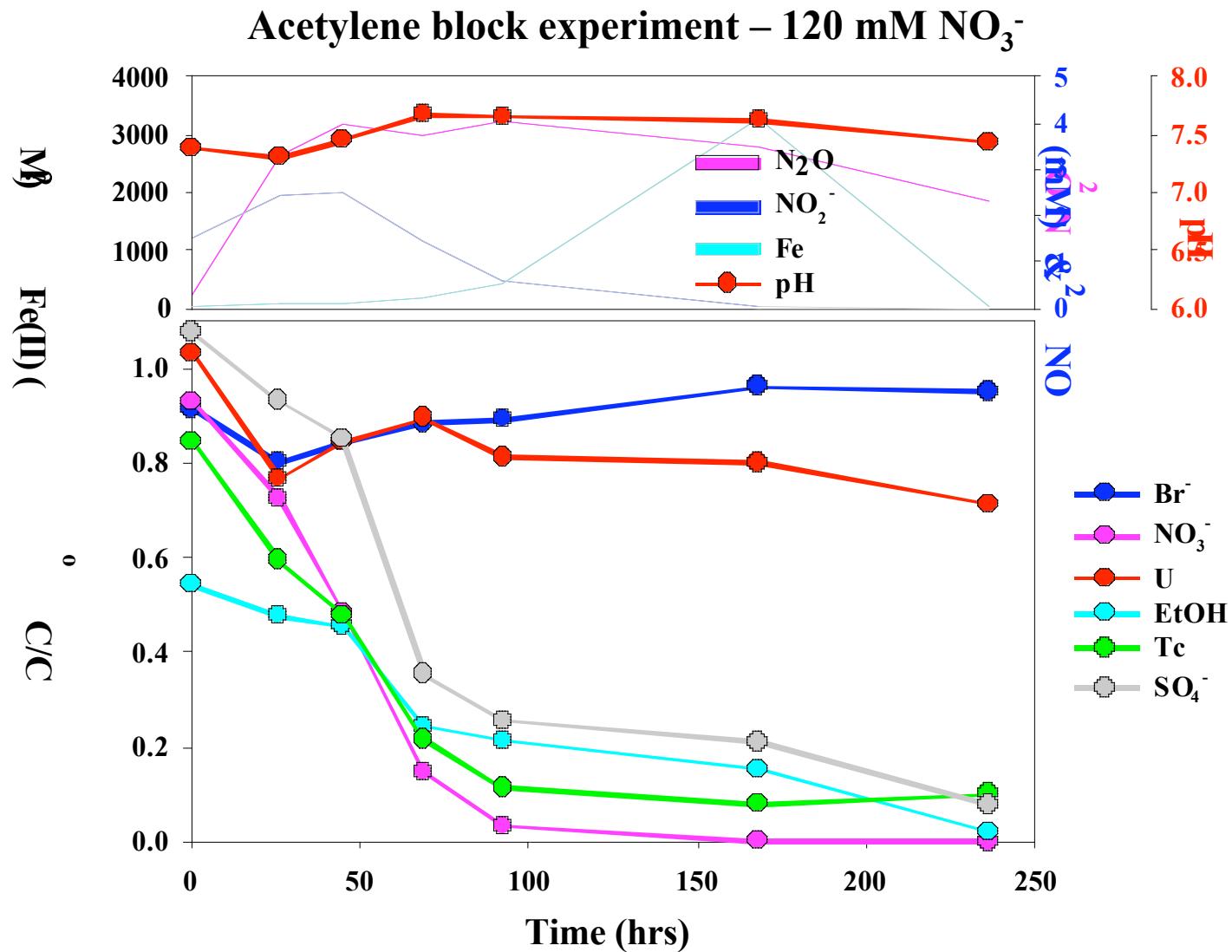
U(VI) reoxidation during denitrification



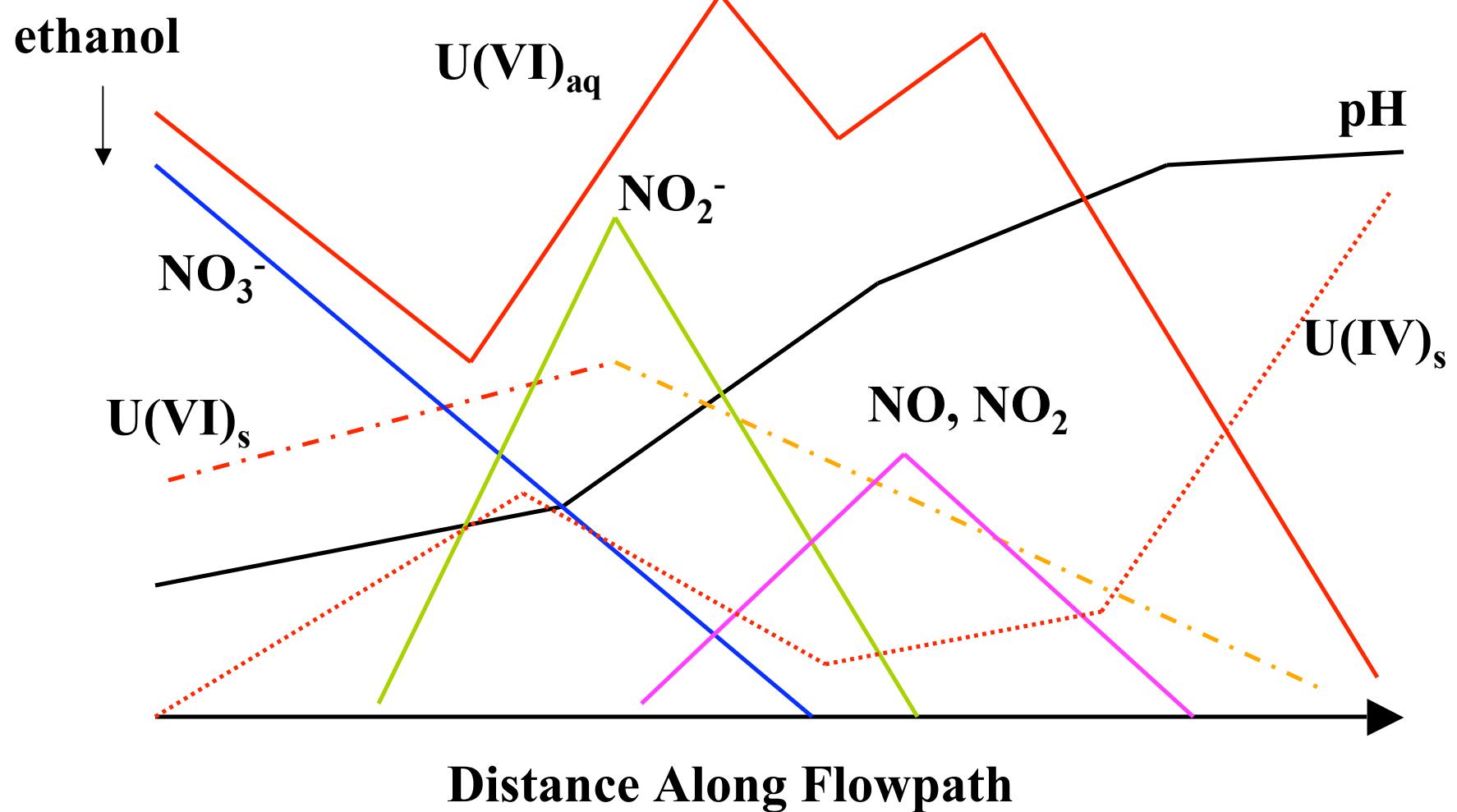
U(VI) reduction following excess sulfide production



Can Acetylene Inhibit Microbial Oxidation of U(IV) ?



Coupled Processes: Bioimmobilization



Point 8: Effectiveness of Bioimmobilization Depends on Coupling Microbial Processes with Physical/Chemical Processes

- Desired metabolic capability is widespread and it may be relatively easy to create subsurface conditions that favor U(VI) reduction
- However, in high nitrate environments, nitrate and denitrification intermediates will rapidly oxidize U(IV)
- pH increases resulting from biostimulation will result in formation of U(VI)-containing solids
- Clogging of aquifer by precipitates, biomass, and (perhaps) N₂ gas is likely in the long-term

Research Strategies

- In situ testing to obtain rates of U(VI) reduction and U(IV) oxidation
 - Physical/chemical heterogeneity
 - Complex geochemistry of site groundwater
- Intermediate-scale laboratory experiments to evaluate and optimize coupled processes
 - 2D and 3D flow paths (donor delivery, pH, biomass, and N₂ clogging issues)
 - Strategies for spatially separating denitrification and U(VI) reduction
 - Strategies for reducing rates of U(IV) oxidation (amendments with sulfate, acetylene, etc.)